



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 664 317 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 94200102.5

(51) Int. Cl.⁶: **C08K 7/26, C08L 23/08**

(22) Date of filing: **19.01.94**

(43) Date of publication of application:
26.07.95 Bulletin 95/30

(84) Designated Contracting States:
GB

(71) Applicant: **DU PONT DE NEMOURS
INTERNATIONAL S.A.
2, chemin du Pavillon,
P.O. Box 50
CH-1218 Le Grand-Saconnex (Genève) (CH)**

(72) Inventor: **Trouilhet, Yves
4b, Chemin des Tattes
CH-1222 Vesenaz,
Geneva (CH)**

(54) **Deodorized thermoplastics.**

(57) A thermoplastic composition comprising (a) a thermoplastic selected from the group consisting of ethylene/acid copolymers and corresponding ionomers; and ethylene/acid/acrylate terpolymers and corresponding ionomers; and (b) an adsorption agent is disclosed, which may be formed into films and shaped articles demonstrating reduced levels of offensive odours and flavours.

EP 0 664 317 A1

Background of the Invention

The present invention relates to the field of thermoplastic compositions suitable for extrusion into films and moulding into shaped articles, more particularly to such compositions containing adsorbents adapted to 5 inhibit offensive odours and flavours of such films and shaped articles.

Background of the Invention

Many films and shaped articles adapted for packaging applications have the unwanted characteristic of 10 possessing undesirable odours and flavours. Such odours and flavours may make the packaging unsuitable for various applications, e.g. in the area of food or hygienic packaging or, in general, any packaging with which man comes into contact. Typically, these undesirable odours and flavours are generated during production of the film or shaped article, e.g. during the extrusion or moulding process.

Various solutions have been proposed for eliminating or inhibiting odours and flavours in thermoplastic 15 films. Adsorbents such as zeolites, diatomaceous earth, clays, activated carbons and the like have been incorporated into certain polymer or copolymers with varying results (cf. e.g. WO 92/13029, WO 92/13899, JP 62032-144, JP 63151-451 and JP 02208-346).

It has now been found that various adsorbents will not only inhibit odours and flavours in particular 20 thermoplastics, but also, that such adsorbents will have a surprising, beneficial effect on various performance characteristics, such as adhesion, heat seal strength and hot tack strength of the films produced from thermoplastic compositions containing the adsorbents.

Summary of the Invention

25 The instant invention relates particularly to a thermoplastic composition comprising (a) a thermoplastic selected from the group consisting of ethylene/acid copolymers and corresponding ionomers; and ethylene/acid/acrylate terpolymers and corresponding ionomers; and (b) an adsorption agent; to thermoplastic films and shaped articles obtainable from this composition; and the use of adsorbents in adsorbing odours and flavours in the aforementioned thermoplastics.

30 As used herein, terms used have the following meanings.

Ethylene/acid copolymer and their corresponding ionomers are well known in the art to be copolymers of ethylene with an olefinically unsaturated organic acid such as acrylic or methacrylic acid, the acid comprising about 0.5 to 50 mole percent of the total polymeric material. The ethylene/acid copolymers and their methods of preparation are well known in the art and are disclosed in, for example US. Pat. Nos. 35 3,264,272, 3,404,134, 3,355,319 and 4,321,337. The copolymers are termed ionomers when the acid is neutralized in whole or in part to produce a salt. The cation for said salts are usually an alkali metals such as sodium or potassium or is zinc or the like.

Ethylene/acid/acrylate terpolymers and corresponding ionomers are well known in the art to be copolymers of ethylene, an olefinically unsaturated organic acid such as acrylic or methacrylic acid and an 40 alkyl acrylate or methacrylate termonomer (e.g. n-butyl acrylate or methacrylate or isobutylacrylate).

Preferred thermoplastics are ionomers that are copolymers of ethylene and 2 to 50%, more preferably 5 to 25%, by weight acrylic or methacrylic acid neutralized up to about 90%, more preferably from 5 to 60% with an alkali metal ion or a divalent or trivalent metal ion, the melt index of the copolymer, whether neutralized or unneutralized, being about 0.1 to 30, preferably 0.5 to 20, dg/min. according to ASTM 45 Standard D1238 (condition E).

Suitable acid copolymers and ionomers are available from the DuPont Company under the trade names Nucrel® and Surlyn®, respectively.

Adsorption agents are known per se. Suitable such agents include powders of diatomaceous earth, clay, kaolin, talc, bentonite, activated carbon and zeolites. Preferred adsorption agents are zeolites, and in 50 particular siliceous molecular sieves.

Suitable siliceous molecular sieves are known in the art, see e.g. European Patent 0 297 543 B1, and have a framework in which at least 90% of the tetrahedral oxide units are SiO₄ tetrahedra, have a pore diameter greater than 5.5 Angstroms (preferably at least 6.2 Angstroms) and have a sorption capacity for water of less than 10 % by weight at 25 °C and 4.6 torr (preferably less than 6 % by weight).

55 Preferred such sieves will have a framework SiO₂/Al₂O₃ molar ratio greater than 35, more preferably 200 to 500.

Suitable siliceous molecular sieves are available under the tradename Abscents® from UOP.

The amount of adsorbent in the polymer or copolymer composition according to the invention will depend upon various factors including the particular copolymer or terpolymer used. Typically the adsorbent agent will comprise at least 0.5% by weight of the composition, more typically 0.5 to 2.0 % by weight of the composition as employed in the end product (film or shaped article) and up to about 30% by weight in the case of a "masterbatch" of composition.

In addition to the above-mentioned composition components, the thermoplastic composition of the present invention may further contain other additional polymeric components as well as the usual additional ingredients and additives conventionally employed in the art for various purposes in polymer compositions, such as, for example, dyes, pigments, fillers, anti-oxidants, fire-retarding agents, etc. When such optional ingredients are employed, their usage is generally in the content range or loading level typically utilized in the art for such purposes.

Films and shaped articles according to the invention can be made by conventional methods, e.g. extrusion coating, blown and cast film processing and injection moulding.

15 Examples

Compositions containing Surlyn® 1652 and various levels of Abscents® 3000 are blended and extruded onto an aluminium foil (38 microns thick) to yield a 25 g/m² of coating of Surlyn® 1652, under the following conditions.

20 Extruder: Egan 3 1/2", L/D = 30

Temperatures from feed to final zone: 175 °, 210 °, 245 °, 265 °, 285 °C

Speed: 53 rpm (max - 270 rpm)

Pressure: 59 bar

Die temperature: 285 °C

25 Air gap: 125 mm

Line speed: 100 m/min

Table 1

30

Extrusion Coating processability		
Composition	total neck-in (mm)	drawability (m/min)
Surlyn® 1652	65	250
Surlyn® 1652 + 0.5 % Abscents® 3000	65	290
Surlyn® 1652 + 2.0 % Abscents® 3000	55	260

35

Total "neck-in" (on both edges) is measured under the processing conditions given above. Total neck-in refers to the difference in width between the extrusion die and the the coating it produces. It is preferable to minimize neck-in so that coatings have a consistent, uniform width and edge.

Drawability is measured by leaving the extruder rpm at the setting giving 25 g/m² coating at 100 m/min and increasing the line speed until edge-weave of the coating is first observed. High drawability is desirable as it enables high line speeds and therewith improved efficiency of a coating operation.

40

Films and shaped articles produced from the compositions according to the invention have been found to have extremely low levels of carboxylic acids and aldehydes, which are known sources of odours.

Odour Analysis

45

Films extruded onto aluminium foils (as previously described) are heated to 70 °C for one hour.

50

Volatiles produced are trapped in an adsorption tube, Tenax GC (5 mm diameter, 100 mm long) at -15 °C, desorbed under rapid heating at 200 °C (within 50 seconds) and introduced in a gas chromatograph (Hewlett Packard Model 5890A) for separation. The volatiles are then introduced in a mass spectrometer for identification and respiration in parallel to detect the odour-producing components. As indicated in Table 2, the concentration of such strong odour-producing components such as butyric acid, 2-methyl butyric acid, 55 valeric acid, pentanal and hexanal, is greatly reduced.

Table 2

Volatile				Volatile (parts per hundred)			
		Surlyn® 1652		Surlyn® 1652 + 0.5 % Abscents® 3000		Surlyn® 1652 + 2.0 % Abscents® 3000	
carboxylic acid							
10	acetic	57		57		32	
	propionic	135		86		6	
	butyric	12		4		-	
	2-methyl butyric	629		199		7	
	valeric	7		-		-	
	caproic	4		-		-	
aldehyde							
20	formaldehyde	19		13		15	
	acetaldehyde	30		36		41	
	propionaldehyde	8		8		10	
	butyraldehyde	9		7		4	
	pentanal	33		19		-	
	hexanal	32		11		-	

25 Samples of Surlyn® 1652 coated onto aluminium foil as previously described are tested for odour and taste.

In the odour test, 4 inch by 4 inch (10.2 cm by 10.2 cm) samples are stored in a sealed jar at 40 °C overnight. The samples are afterwards cooled for 1 hour before testing for odour. The samples are rated for intensity of odour on a scale of 1 to 8, with 1 being weakest and 8 being strongest intensity of odour.

30 In the taste evaluation, samples are formed into an 8.5 inch by 11 inch (21.6 cm by 27.9 cm) pouch and filled with 85 °C water. The pouches are stored at room temperature overnight. The water stored in the pouches is rated for intensity of taste on a scale of 1 to 8, with 1 being weakest and 8 being strongest intensity of taste.

Table 3

taste and odour evaluation							
		Surlyn® 1652		Surlyn® 1652 + 0.5 % Abscents® 3000		Surlyn® 1652 + 2.0 % Abscents® 3000	
Flavour							
40	overall	3.5		2.0		2.0	
	vinyl	3.0		0		0	
	bitter	0		0		1.0	
	metallic	0		1.0		0	
Odour							
45	overall	3.5		1.0		3.0	
	Polyethylene	1.5		0		2.0	
	sweet plastic	0		1.0		0	
	smoky/rubber	2.0		0		0	
	smoky/musty	0		0		2.0	
	musty	1.0		0		0	

55 In addition to having inhibited or eliminated undesirable odours and flavours, the thermoplastic compositions according to the invention have been found to possess surprising improvements in performance characteristics. Depending upon the particular end-use application, it can be critical that the film

possess a certain level of adhesion to a foil (e.g. aluminium foil) and sealing properties.

Adhesion to foil

5 Adhesion to an aluminium foil of thickness 38 μ m is tested using film samples produced by the extrusion coating process previously described. Extruder temperatures are as previously mentioned, except that for compositions based on Surlyn® 1702, the extruder temperature is, from feed to final zone 150 °, 170 °, 200 °, 220 °, 230 °C, and the die temperature is 230 °C.

10

Table 4

Adhesion to Foil (100 mm/mn cross head speed)		
Composition		Adhesion (N/15 mm)
15	Surlyn® 1652	4.1
	Surlyn® 1652 + 0.5 % Abscents® 3000	4.1
	Surlyn® 1652 + 2.0 % Abscents® 3000	4.5
20	Surlyn® 1702	6.0
	Surlyn® 1702 + 0.5 % Abscents® 3000	6.2
	Surlyn® 1702 + 2.0 % Abscents® 3000	6.6

Heat Seal Strength

25

Film samples are sealed on a KOPP heat sealer at a 1.0 sec dwell time and 0.5 MPa pressure. The seal strength is measured at 100 m/min cross head speed, according to ISO 9001 work instruction T91 of P&IP ETC, Meyrin.

30

Table 5

Heat Seal Strength (N/15 mm)			
Seal Bar Temp. (°C)	Surlyn® 1652	Surlyn® 1652 + 0.5 % Abscents® 3000	Surlyn® 1652 + 2.0 % Abscents® 3000
35	80	0.8	0.8
	100	9.5	12
	120	11	11

40

Hot-Tack Strength

45 The hot-tack strength of a film is a measure of the strength of a seal made with the film at a given temperature. High hot-tack strength is desirable since the need for cooling seals during, e.g. a packaging process is reduced or eliminated and packaging rates can thereby be increased. The hot-tack strength of samples is measured using a PACKFORSK hot-tack tester run at 0.3 MPa dwell pressure, 0.5 sec dwell time, 0.2 sec delay time and 150 mm/sec cross head speed, according to ISO 9001 work instruction T92 of P&IP ETC, Meyrin.

50

55

Table 6

Hot-Tack Strength (N/15 mm)				
5	Seal Bar Temp. (°C)	Surlyn® 1652	Surlyn® 1652 + 0.5 % Abscents® 3000	Surlyn® 1652 + 2.0 % Abscents® 3000
10	70	-	0.2	0.3
	80	0.5	1.0	0.8
	90	0.6	2.8	1.0
	100	4.5	8.0	7.0
	110	9.0	9.0	9.0

15 **Claims**

1. A thermoplastic composition comprising (a) a thermoplastic selected from the group consisting of ethylene/acid copolymers and corresponding ionomers; and ethylene/acid/acrylate terpolymers and corresponding ionomers; and (b) an adsorption agent.
- 20 2. A composition according to claim 1 wherein component (a) comprises a copolymer of ethylene and acrylic acid or methacrylic acid and corresponding ionomers; a terpolymer of ethylene, acrylic acid or methacrylic acid and an alkyl acrylate or methacrylate, and corresponding ionomers.
- 25 3. A composition according to claim 2 wherein component (a) is a copolymer of ethylene and 2 to 50% by weight acrylic or methacrylic acid neutralized up to about 90%.
4. A composition according to claim 3 wherein component (a) is a copolymer of ethylene and 5 to 25% by weight acrylic or methacrylic acid neutralized from 5 to 60%.
- 30 5. A composition according to any one of claims 1 to 4 wherein the adsorption agent is a crystalline siliceous molecular sieve.
- 35 6. A composition according to any one of claims 1 to 5 wherein the crystalline siliceous molecular sieve has a framework in which at least 90% of the tetrahedral oxide units are SiO₄ tetrahedra, has a pore diameter greater than 5.5 Angstroms and has a sorption capacity for water of less than 10 % by weight at 25 °C and 4.6 torr.
7. A composition according to claim 6 wherein the crystalline siliceous molecular sieve has a framework SiO₂/Al₂O₃ molar ratio greater than 35.
- 40 8. A composition according to any one of claims 1 to 7 wherein the adsorption agent comprises at least 0.5 % by weight of the composition.
- 45 9. A thermoplastic film obtainable by extruding the composition according to any one of claims 1 to 8.
10. A thermoplastic shaped article obtainable by moulding the composition according to any one of claims 1 to 8.
- 50 11. The use of an adsorbent to inhibit odours or flavours in films and shaped articles formed from a thermoplastic, the thermoplastic comprising an ethylene/acid copolymer or corresponding ionomer or an ethylene/acid/acrylate terpolymer or corresponding ionomer.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 0102

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<p>DATABASE WPI Week 8542, Derwent Publications Ltd., London, GB; AN 85-261191 & JP-A-60 176 659 (TOPPAN PRINTING KK) 10 September 1985 * abstract *</p> <p>---</p>	1,2,5	C08K7/26 C08L23/08
A,D	<p>WO-A-92 13029 (NESTE OY) * page 3, line 21 - line 24 * * page 6, line 8 - line 13 * * claims 1-4,6 *</p> <p>---</p>	1,5-8,11	
A	<p>EP-A-0 395 104 (UCC) * page 2, line 34 - line 35 * * page 2, line 40 - line 42 * * page 3, line 1 - line 8 * * claims 1,4-6 *</p> <p>---</p>	1,5,6,8, 11	
A	<p>US-A-4 833 181 (K.NARUKAWA ET AL.) * column 1, line 48 - line 52 * * column 2, line 53 - line 58 * * page 4, line 42 - line 49 * * claims 1,15,16 *</p> <p>-----</p>	1,2,5,8	<p>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</p> <p>C08K</p>
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	9 June 1994	Engel, S	
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>	

